Eugene Wilusz[1] and Kyle D. Hassler[1]

CHEMICAL RESISTANCE PROPERTIES OF ADVANCED GLOVE MATERIALS

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ABSTRACT: Butyl rubber has been used for many years in chemical protective clothing applications such as gloves, overboots, and coated fabrics used in ensembles for the military and also used in industry. Novel compounds and material configurations have been developed for improved chemical protective gloves based on butyl rubber. The materials were challenged with toluene, 2,2,4- trimethylpentane, 1,5-dichloropentane, and triethyl phosphate. Because of the chemical specific nature of barrier properties, a two-layer approach using elastomers having different solubility parameters was used to provide resistance to hydrocarbons as well as to polar liquids. Poly-(epichlorohydrin)/butyl rubber gloves demonstrated a combination of chemical resistance properties for both hydrocarbons and other chemical hazards. Flame-retardant formulations of butyl rubber were developed using a suitable combination of additives. Gloves from the flame-retardant formulations provide the same barrier properties against the chemicals tested as standard butyl gloves.

KEYWORDS: butyl, flame-retardant, two-layer, hydrocarbon liquids, polar liquids, permeation

Protective gloves are an important component of ensembles designed to provide protection from exposure to hazardous chemicals. Such gloves are commonly made from elastomeric materials although

[1]Chief, and chemist, respectively, Materials and Polymer Applications Branch, Individual Protection Directorate, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5019.

other air impermeable polymeric materials, such as thermoplastic films, are also used. Protective gloves made from butyl, neoprene, nitrile, and Viton[R] elastomers are commercially available and in widespread use in industry. Generally, such gloves provide excellent protection against a range of classes of chemicals while being susceptible to permeation by other chemicals. One type of glove used by the military for chemical protection is made from butyl rubber, which has also been used for many years in overboots and coated fabrics for ensembles.

Butyl rubber is made by the copolymerization of isobutylene with about two percent isoprene. The isoprene component provides sites of unsaturation that are used in vulcanizing the rubber. The isobutylene-based structure of the rubber is responsible for its useful barrier properties against gases, moisture, and liquid chemicals, making it a widespread choice as an impermeable material.[1] This barrier property is illustrated in the early use of butyl rubber for many years as inner tubes for tires.

The permeation of a chemical through a barrier material is a multistep process involving the sorption of the chemical into the surface of the barrier, diffusion through the barrier, and desorption from the other surface. Properties of importance in considering this process include the solubility of the chemical in the barrier material as well as the diffusion coefficient.[2] The solubility parameter is a thermodynamic property which is commonly used in studies of the affinity of chemicals for dissolving in other chemicals. The solubility parameter of butyl rubber is approximately 16 $(J/cc)^{1/2}$.[3] Many hydrocarbon liquids have solubility parameters near this value (14-18) [3,4] and hence are highly soluble in butyl rubber, causing a swelling of the elastomeric network structure upon contact. Other liquid chemicals have quite different cohesive energy densities, and hence different solubility parameters (outside the range 14-18). These chemicals are generally more polar liquids and have much less affinity for butyl rubber. Butyl is a highly effective barrier against such liquid chemicals.

Butyl rubber gloves of 0.64 mm (0.025 in.) thickness have been used in the military for many years to provide protection against hazardous chemicals. These gloves have served their purpose well over the years. However, in order to carry out certain fine tasks, greater tactility is required. Furthermore, butyl gloves are also susceptible to attack by petroleum products, and butyl rubber is inherently flammable.[5] Care must therefore be exercised in using butyl gloves in the presence of these latter two hazards. Work therefore was undertaken with the objective of extending the protection afforded by butyl rubber gloves to all of the aforementioned hazards.

EXPERIMENTAL

Improvements in tactility were introduced by developing a 0.36 mm (0.014 in.) and a 0.18 mm (0.007 in.) version of the standard butyl gloves. Therefore, butyl rubber gloves are now available in three nominal thicknesses of 0.18 mm (0.007 in.), 0.36 mm (0.014 in.), and 0.64 mm (.025 in.). All of the gloves studied in this work were prepared by a dipping process.

Resistance to petroleum products was introduced by using a two-layer approach. An oil resistant elastomer, epichlorohydrin-ethylene oxide copolymer (ECO), was used as the outer layer in a composite with butyl rubber (IIR) as the inner layer. Sheets were prepared by mixing on a two-roll mill followed by compression molding and curing in a press.

Flame retardance was introduced first into butyl rubber sheets using additives during compounding. Mixing was carried out on a two roll mill. Sheets were prepared by compression molding. Prototype gloves were prepared by dipping.

The various gloves and materials were subjected to challenge by 1,5-dichloropentane (DCP); triethyl phosphate (TEP); 2,2,4-trimethylpentane (iso-octane); and toluene. Barrier properties were determined according to ASTM Method F739-85. A 2-inch ASTM permeation test cell was used in all cases. Each test was performed in triplicate. A constant temperature bath was used to maintain the temperature at 25^{o}C. Liquid collection was used on the downstream side of the cell. The collection medium was distilled water for TEP experiments; 2-propanol for DCP, iso-octane, and toluene with butyl materials; and hexane with DCP, iso-octane, and toluene with ECO materials.

A fully flooded surface was obtained on the upstream side of the cell using 60 mL of challenge liquid. At timed intervals, 600 uL was withdrawn from the collection side using an automatic pipette and placed into an autosampler vial. The 600 uL was then replaced with fresh collection liquid. Perkin-Elmer gas chromatographs (Models SIGMA 300 and 8410) equipped with flame ionization detectors were used to analyze the aliquots. Gas chromatographs were equipped with autosamplers. Data reduction was achieved through a Perkin-Elmer Integrator Model LCI 100. Breakthrough times were recorded as the last interval before component detection. Minimum detection limit was 0.5 ppm. Steady-state permeation rates were determined from the slope of the straight line portion of the breakthrough curves.

RESULTS AND DISCUSSION

Effect of Thickness

The standard 0.64 mm (0.025 in.) butyl rubber glove shows good barrier properties against DCP and TEP as shown in Table 1. Two additional thicknesses, 0.18 and 0.36 mm (0.007, 0.014 in.), were also tested. The 0.18 mm glove performed well against TEP, but the 0.36 mm glove did considerably better with 145 and 7060 minutes breakthrough times against DCP and TEP, respectively. The results of the permeation experiments, as shown in Fig. 1, clearly demonstrate that thickness has a very important effect on the breakthrough time of the component. This phenomenon is not exclusive of butyl. It is also demonstrated in the different thicknesses of the ECO sheets. Within a material type, thickness has a primary effect on the challenge breakthrough time.

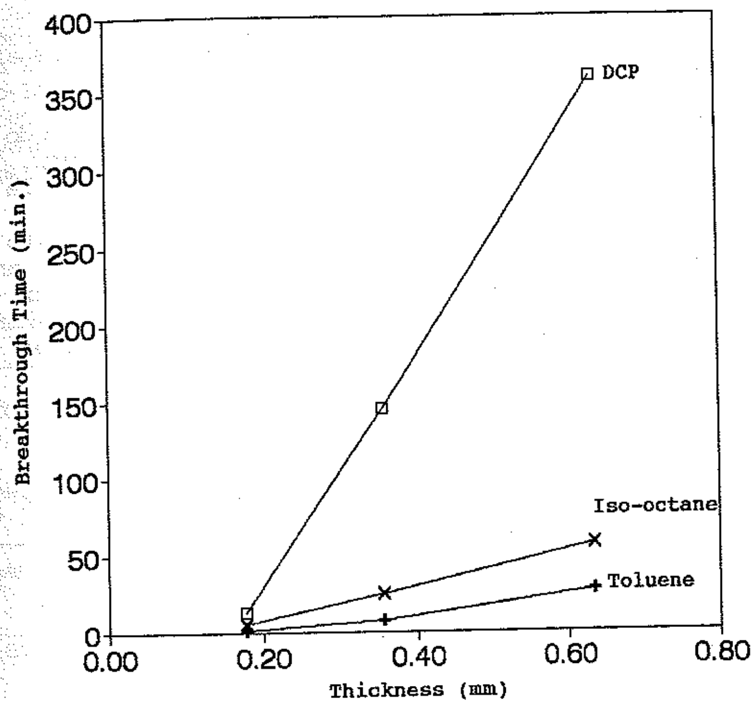

FIG. 1 -- Breakthrough time versus glove material thickness

Effect of Material Type

Material thickness can become overshadowed when introducing material differences, specifically in addressing the breakthrough behavior of the 0.18 and 0.36 mm butyl and ECO material/challenge combinations. An analysis of co-variance (ANCOVA) was performed using the breakthrough times as the dependent variable and the thickness as the covariant.[6] Because the covariant is not significant, the emphasis becomes the breakthrough time responses as a result of the unique combinations of material and challenge ($p < 0.01$). See Appendix A for ANCOVA table. Therefore the breakthrough time study investigated the challenge/material combinations with a direction to reduce the necessary thickness of the materials for acceptable barrier properties. For this reason the 0.64 mm butyl gloves are eliminated from the focus of further discussion.

A two-way analysis of variance (ANOVA) of glove types and challenges supported the two-variable interaction phenomenon. See Appendix B for ANOVA table. Two gloves were relatively superior to the other three materials for barrier protection. The 0.36 mm butyl and the 2-layer gloves showed longer absolute breakthrough times.Additional analysis of breakthrough times versus individual challenges also indicated that these two materials performed relatively better than the others.

By eliminating the effect of the lower response time materials a subsequent ANOVA again supported the significance of unique breakthrough times for the material/challenge combinations ($p < 0.01$). This means that the glove type and challenge liquids do not contribute independently to the observed breakthrough behavior. Therefore the effect of each variable on breakthrough time cannot be determined separately. Further comparison by challenge type is presented in Table 2. Significant differences exist at the $p = 0.05$ level between the two gloves when they were subjected to DCP, TEP, and iso-octane. In the cases of DCP and TEP the butyl glove was better, however, the 2-layer was superior when subjected to iso-octane. There was no difference between the response times of the two gloves when challenged with toluene.

TABLE 1 -- Breakthrough times (mins.)[a] (25°C)

Material	Challenge Chemical			
	DCP	TEP	Toluene	Iso-octane
Butyl (0.18 mm)	13	1710	1	5
Butyl (0.36 mm)	145	7060	7	25
Butyl (0.64 mm)	360	>15,420	27	57
ECO (0.18 mm)	4	8	3	110
ECO (0.36 mm)	8	15	8	330
2-layer (0.36 mm)	35	4020	9	670

[a]Average of 3 replicates

The 2-layer ECO/butyl glove has 0.13 mm (0.005 in.) of ECO and 0.23 mm (0.009 in.) of butyl which will probably cause a trade-off in some aspects of barrier effectiveness. In this case the trade-off manifested itself in a 75% decrease in breakthrough time against DCP from butyl to the 2-layer glove. ECO does not have the same resistance to DCP as butyl. Therefore that layer would not be expected to add as much to the barrier properties against this challenge. The thinner layer of butyl is probably the larger factor contributing to the lowered breakthrough time. Given the range of variation in the nominal thickness classifications, it would be appropriate to compare the breakthrough times of the 0.18 mm butyl and the 2-layer gloves. Thirty five minutes breakthrough time for the two-layer glove is an improvement in barrier protection over the 13 minutes for the 0.18 mm butyl glove. Furthermore, this improvement is beyond the 0.18 mm butyl breakthrough time being additive with the 4 minutes, 0.18 mm ECO, breakthrough time.

TABLE 2 -- Comparison of 2-layer and 0.36 mm Butyl Materials Breakthrough Time (mins.)

Material	Challenge Chemical			
	DCP	TEP	Toluene	Iso-octane
Butyl (0.36 mm)	145	7060	7	25
2-layer (0.36 mm)	35	4020	9	670
Change in BT (%)	-76[a]	-43[a]	+29	+2580[a]

[a] Significant difference between the glove materials at $p = 0.05$.

The difference in breakthrough time between the 0.36 mm butyl and the 2-layer glove for TEP is statistically significant, but "significantly" different might be an academic point when viewing the data from a practical application aspect. For the former glove, 7060 minutes translates into 117 hours, and 4020 minutes equals 67 hours for the latter. This type of difference is really not pragmatic because 67 hours exceeds any normal work exposure conditions. Therefore, these two gloves are considered excellent barriers versus this challenge.

In the case of toluene challenge, neither material is a very good barrier. This fact is illustrated by the statistical analysis and the absolute breakthrough values in the 7 to 9 minutes range. (See Table 2) Aromatic hydrocarbon compounds such as benzene, toluene, or xylenes, are found in some fuels. For current glove applications, this type of exposure is generally minimal. Furthermore these liquids are volatile, and evaporate quite rapidly following an accidental splash. Of greater probability of prolonged contact are persistent greases and oils made up largely of aliphatic hydrocarbons. The two gloves performed quite differently when subjected to iso-octane. Breakthrough time for the butyl was 25 minutes compared to 670 minutes for the 2-layer. This difference clearly illustrates the positive barrier property of the ECO layer over butyl. This represents an extremely large increase in breakthrough time by adding the 0.13 mm ECO layer over the 0.23 mm butyl as compared to the 0.36 mm butyl standard. The increase is even greater, of course, when compared with the 0.18 mm butyl.

To validate these findings and demonstrate practical application, hydrocarbon contamination experiments with subsequent TEP exposure were performed. Hydrocarbon contact was 5 minutes full surface exposure to a liquid mixture containing 70% iso-octane and 30% toluene (ASTM D471-79 Fuel B). After the exposure, the samples were drained and allowed to dry for 30 minutes; TEP challenge followed. These steps were performed while the sample was clamped in the ASTM permeation cell. Butyl rubber glove material, 0.36 mm, challenged in this manner had breakthrough times consistently less than 5 minutes. This indicates that this exposure rendered the butyl ineffective for subsequent chemical challenge. In an analogous experiment the 2-layer glove resisted permeation for approximately 135 minutes. Breakthrough then was observed, followed by a relatively high permeation rate, subsequently settling to a lesser steady state permeation rate. The contrasting results from these hydrocarbon contamination experiments demonstrate the effectiveness of the ECO layer in providing an effective barrier under these circumstances.

In summary, the chemical resistance properties of the 2-layer glove are a compromise between the properties of the individual material components. The 2-layer composite affords protection to DCP that is less than the 0.36 mm, but more than the 0.18 mm, butyl standard; adequate protection against TEP; and greatly improved protection against iso-octane. The compromise is justified when hydrocarbon contamination is likely.

Effect of Flame Retardant Additives

Because butyl rubber is primarily polyisobutylene, a polymerized hydrocarbon, it is inherently flammable. A piece of the glove subjected to an open flame readily ignites, rapidly burns, and sustains the flame after the source has been removed. The flame retardant (FR) glove samples demonstrated improved flammability properties. Samples subjected to an open flame were difficult to ignite and self-extinguished after the source was removed.

Two thicknesses (0.36, 0.64 mm) of gloves were permeation tested, then compared to similar thicknesses of standard butyl gloves to determine if the FR additives had negatively affected the original barrier properties. Results from the experiments are presented in Table 3. Thickness of the gloves played a larger role in breakthrough times than did material type. Breakthrough times for the 0.64 mm FR glove are longer than those for the 0.36 mm FR glove.

One-way ANOVA analysis of the breakthrough times of the 0.36 mm FR and standard butyl gloves indicate that there is no significant difference ($p > 0.01$) between the breakthrough times when challenged with any of the four chemicals. A large difference between the breakthrough times to TEP did not indicate a significant effect, due to material type, possibly because of the breakthrough time variabilities within each group of material.

The 0.64 mm glove results followed the same pattern as found with the 0.36 mm, reaffirming the absence of a negative effect of FR additives on the breakthrough times. Breakthrough times for TEP were excessively long, and these experiments were either terminated before breakthrough or not performed. Therefore data for this challenge was not included in the analysis.

TABLE 3 -- Breakthrough Times (mins.) for Butyl Material (25°C)

Material	Challenge Chemical			
	DCP	TEP	Toluene	Iso-octane
Butyl (0.36 mm)	145	7060	7	25
Butyl (0.64 mm)	360	>15,420	27	57
FR Butyl (0.36 mm)	120	10,020	8	13
FR Butyl (0.64 mm)	390	...	20	53

CONCLUSIONS

Advanced glove materials having useful chemical resistance properties have been developed. Two-layer ECO/butyl rubber gloves provide a combination of chemical resistance properties for situations where exposure to petroleum based fuels, oils and lubricants is a concern in addition to other chemical hazards.

Flame retardant butyl rubber gloves provide the same barrier properties against the chemicals tested as standard butyl gloves. The use of FR additives in the butyl formulation does not adversely affect barrier performance.

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APPENDIX A -- Analysis of Co-Variance Table

Source	df	SS	MS	F	p>F
Thickness	1	6260.758	6260.758	0.33	0.5695
Glove Type	4	1.9882E07	4970541	261.38	<0.01
Challenge	3	6.8281E07	2.2760E07	1196.87	<0.01
Glove*Challenge	12	7.8734E07	6561171	345.02	<0.01
Error	38	722637.3	19016.77		
Total	58	1.7864E08			

APPENDIX B -- Analysis of Variance Table

Source	df	SS	MS	F	p>F
Glove Type	4	2.7941E07	6985432	373.76	<0.01
Challenge	3	6.8281E07	2.2834E07	1221.77	<0.01
Glove*Challenge	12	8.0736E07	6728021	359.99	<0.01
Error	38	728898	18689.69		
Total	58	1.7864E08			

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